201-15852

HERCULES

Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, DE 19808-1599
(302) 995-3000
www.herc.com

January 18, 2005

RECEIVED
OPPT CBIC
05 APR -4 PM 1:31

Ms. Karen S. Hoffman
U.S. Environmental Protection Agency
7405M USEPA Headquarters, Ariel Rios Building
1200 Pennsylvania Avenue, N. W.
Washington, DC 20460

Dear Karen:

This is a follow up to several communications that we have had regarding Hercules' HPV Challenge commitment to CASRN: 68955-37-3; acid chlorides, tallow, hydrogenated. Hercules had sent a memo to Mr. Charlie Auer on 21-Apr-04 (see Attachment 1, your doc #201-15258) regarding status of this HPV chemical. In response, you sent an e-mail date 23-June-04 (see Attachment 2) indicating that the information Hercules sent to Mr. Auer was not relevant to CASRN 68955-37-3. relevant to this HPV substance. You are correct and I apologize for the confusion. Please disregard our 21-Apr-04 letter to Mr. Auer as it is not relevant to CASRN 68955-37-3, but rather to the end product produced from that intermediate.

After further research into the guidelines and intent of the HPV program, as well as review of our own manufacturing process for CASRN 68955-37-3, Hercules respectfully wishes to withdraw its commitment to test this material. Our reasoning is based on two arguments:

1. Hercules feels that it was incorrectly identified as an isolated intermediate. You will find in Attachment 3, a brief description of the manufacturing process we use to make this intermediate. While it is indeed, a chemical intermediate, it is not stored, isolated or removed from the manufacturing equipment. As such, there is little or no potential for health or environmental exposure.

2. While Hercules feels that reason #1 is sufficient to delete this chemical from the HPV program, we also provide additional information which we hope will help convince EPA that testing of this material would be moot and unnecessary given the health or environmental fate of this type of chemical. We offer this additional information as Attachment 4.

Thank you in advance for your review and consideration in this matter. Please feel free to contact me if you have any questions or comments on this information we have presented.

Sincerely,

G. L. McCallister
Director, Regulatory Affairs

GLM:clj
Attachments

FAC1_HPVletter.doc/1-2

Attachment 1

201-15258

HERCULES

Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, DE 19808-1599
(302) 995-3000
www.herc.com

April 21, 2004

Administrator
U.S. Environmental Protection Agency
P.O. Box 1473
Merrifield, VA 22116

04 MAY 11 PM 12: 40

RECEIVED

Attn: Chemical Right-to-Know Program

RE: Attached letter from Mr. Charles Auer regarding unsponsored chemical

Dear Administrator,

Enclosed is a copy of a recent letter we received from Mr. Charles Auer regarding our participation in the HPV Program. In that letter, Mr. Auer indicates that we have not submitted a test plan for a chemical to which we had originally committed. The chemical is identified in the attachment to that letter.

Please be advised that shortly after we had sent out commitment to EPA in the Fall of 1999, we formed a consortium with several international partners and agreed to sponsor this chemical under the ICCA HPV Program. Also enclosed is a copy of the letter that was sent to Mr. Auer in the Fall of 1999 describing that commitment, the consortium members and the chemicals they were sponsoring.

That program is well advanced at this point in time. SIDS dossier is in preparation. I trust this satisfies your immediate concerns. Should you need additional information, please do not hesitate to contact me.

Sincerely,

G. L. McCallister
Director, Regulatory Affair

GLM:clj
Enclosures

2004letters.doc/9

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

APR 12 2004

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

Mr. G.L. McCallister
Hercules Incorporated
1313 North Market Street
Wilmington, DE 19894-0001

Dear Mr. McCallister:

I want to personally acknowledge and thank you for your commitment to the High Production Volume (HPV) Challenge Program. Participation in the HPV Challenge Program has exceeded EPA's expectations and, although the success of the program has been significant, there are a number of commitments that have not yet been met and are considered late. Preparations are underway for release of the HPV Challenge Program Status Report in May, 2004. The HPV Challenge Program Status Report will identify those sponsors whose commitments are overdue.

Our records indicate that your organization has sponsored the chemical(s) listed in the attached table for a start year of 2003 or earlier but robust summary and test plan information has not been received by the Agency. The commitment start year indicates the year of the Program in which sponsors agreed to begin the evaluation of each chemical by submitting robust summaries of existing data and a test plan showing how the sponsor plans to fill any data gaps. Under the HPV Challenge Program, all test plans and robust summary submissions should be submitted in the year indicated. Any needed new testing on the HPV chemicals in the HPV Challenge Program is to be completed by the end of 2004 with all data to be made available to the public by 2005. So that the Agency may meet its HPV Challenge Program's objectives, we are no longer accepting changes to start years and commitments not yet fulfilled are considered late.

While we are not accepting changes to start years, the Agency does expect sponsors to uphold their commitments and submit test plans and robust summaries as soon as possible. If no test plan/robust summary submission is received before the end of 2004 for these commitments, then the Agency will consider these chemicals as "orphans"—or unsponsored. Chemicals not voluntarily sponsored in the HPV Challenge Program will become candidates for test rules under Section 4 of the Toxic Substances Control Act (TSCA).

The Agency understands that over time, for a variety of reasons, sponsorship plans may change; however, it is incumbent upon sponsors of unmet commitments to update the Agency so that its records may accurately reflect the current commitment status. Information should be sent to:

Administrator
US Environmental Protection Agency
P.O. Box 1473
Merrifield, VA 22116
Attention: Chemical Right-to-Know Program

or through e-mail at: oppt.ncic@epa.gov *and* chem.rtk@epa.gov by April 30, 2004. Please note that any correspondence containing Confidential Business Information (CBI) should not be sent to the above address or through e-mail.

If you have any questions or concerns, please contact Karen Lannon of my staff at 202-564-8163. Thank you.

Sincerely,

Charles M. Auer
Director
Office of Pollution Prevention and Toxics

Attachment

HERCULES INCORPORATED
RECEIVED
APR 1 9 2004
REGULATORY AFFAIRS
AND TOXICOLOGY

Hercules Incorporated — Overdue Commitments

CAS Number	9th Collective Index Name	Start Year
68955-37-3	Acid chlorides, tallow, hydrogenated	2002

GLOBAL PRODUCERS OF AKD

Dr Peter Ungeheuer
Tel : +49-69-2556-1341
Fax : +49-69-2556-1342
e-mail: Ungeheuer@VCI.de

Verband Tegewa
Karlstraße 21
D-60329 Frankfurt

Mr Charles M. Auer
Director, Chemical Control Division
U.S. Environmental Protection Agency
401 M Str., S.W. (7405 Rm E 403)
Washington, DC 20460
USA

November 30 1999
Ung/ot/007

ICCA-Commitment / US HPV Challenge Program

Dear Mr Auer

Please find enclosed for your information the commitment of the task force "Global Producers of AKD" to sponsor Alkylketendimer (AKD) in the frame of the ICCA-HPV-Initiative.

The task force represents the following companies:

- BASF Aktiengesellschaft
- EKA Chemicals AB
- Hercules BV
- Kemira Chemicals Oy
- NOF Corporation
- Raisio Chemicals Oy

Would you be so kind to send us an acknowledgement that AKD is no longer directly a subject of the US-challenge program.

Yours sincerely

Global Producers of AKD

Enclosure

Dr. Peter Ungeheuer

GLOBAL PRODUCERS OF AKD

Dr Peter Ungeheuer
Tel : +49-69-2556-1341
Fax : +49-69-2556-1342
e-mail: Ungeheuer@VCI.de

Verband Tegewa
Karlstraße 21
D-60329 Frankfurt

Fax: +32-2-676-7332

Mr Siva Bushana Rao
Chemical Resources Unit Manager
European Chemical Industry Council
(CEFIC)

November 30 1999
Ung/ot/004

ICCA Commitment for Alkylketendimer (AKD)

Dear Mr Bhushana Rao

On behalf of the producers of AKD in the US, Europe and Japan, namely the companies

- BASF Aktiengesellschaft
- EKA Chemicals AB
- Hercules BV
- Kemira Chemicals Oy
- NOF Corporation
- Raisio Chemicals Oy

we would like to inform you that the above mentioned companies have formed a consortium called

"Global producers of AKD"

to commit themselves to the ICCA HPVC program for AKD.

GLOBAL PRODUCERS OF AKD

Dr Peter Ungeheuer
Tel : +49-69-2556-1341
Fax : +49-69-2556-1342
e-mail: Ungeheuer@VCI.de

Verband Tegewa
Karlstraße 21
D-60329 Frankfurt

Fax: +1-703-741-6098

Mr Frederick C. McEldowney
Product Stewardship Team
Chemical Manufacturers Association
(CMA)

November 30 1999
Ung/ot/004

ICCA Commitment for Alkylketendimer (AKD)

Dear Mr McEldowney

On behalf of the producers of AKD in the US, Europe and Japan, namely the companies

- BASF Aktiengesellschaft
- EKA Chemicals AB
- Hercules BV
- Kemira Chemicals Oy
- NOF Corporation
- Raisio Chemicals Oy

we would like to inform you that the above mentioned companies have formed a consortium called

"Global producers of AKD"

to commit themselves to the ICCA HPVC program for AKD.

GLOBAL PRODUCERS OF AKD

Dr Peter Ungeheuer
Tel : +49-69-2556-1341
Fax : +49-69-2556-1342
e-mail: Ungeheuer@VCI.de

Verband Tegewa
Karlstraße 21
D-60329 Frankfurt

Fax: +81-3-3580-0764

Mr Masatoshi Ogura
General Manager
Task Force Team for ICCA
JCIA

November 30 1999
Ung/ot/004

ICCA Commitment for Alkylketendimer (AKD)

Dear Mr Ogura

On behalf of the producers of AKD in the US, Europe and Japan, namely the companies

- BASF Aktiengesellschaft
- EKA Chemicals AB
- Hercules BV
- Kemira Chemicals Oy
- NOF Corporation
- Raisio Chemicals Oy

we would like to inform you that the above mentioned companies have formed a consortium called

"Global producers of AKD"

to commit themselves to the ICCA HPVC program for AKD.

The commitment covers the following individual substances which will be handled as a family

CAS Reg No	CAS Name
10126-68-8	4-heptadecylidene-3-hexadecyloxetan-2-one
42272-70-8	4-pentadecylidene-3-tetradecyloxetan-2-one
55680-03-0	4-undecylidine-3-decyloxetan-2-one
56000-16-9	(,Z,Z)-4-(heptadec-8-enylidene)-3-(hexadec-7-enyl)oxetan-2-one
67845-94-7	4-heptadecylidene-3-tetradecyloxetan-2-one
67845-95-8	3-hexadecyl-4-pentadecylideneeoxetan-2-one
68390-56-7	Fatty acids, tallow, hydrogenated, dimers, diketene derivates
68556-25-2	1,9-Octadecadien-1-one, (Z)-, dimer
84989-41-3	2-Oxetanone, 3-C12-16-alkyl-4-C13-17-alkylidene derivs.
94109-14-5	2-heptadecylidene-4-hexadecyloxetan-3-one
98246-87-8	2-Oxetanone, 3-C14-16-alkyl-4-C15-17-alkylidene derivs.

The necessary testing will start in the year 2000.

The undersigned will act as contact point.

Kind regards

Global Producers of AKD

Dr Peter Ungeheuer
Vice-Director Association TEGEWA e.V.

Attachment 2

Hoffman.Karen@epamail.epa.gov

06/23/2004 02:00 PM

To: gmccalister1@herc.com
cc: cjenkins@herc.com, rhartgrove@herc.com
Subject: Question concerning your letter to EPA Administrator re: CAS 68955-37-3

Dear Mr. McCallister:

We received your letter of April 21, 2004. (see attached pdf file below) in response to a letter from Charles Auer concerning Hercules' sponsorship of CAS 68955-37-3. In your letter, you attached a previous letter sent in the fall of 1999 giving a list of your chemicals that were now going to be sponsored under the Global Producers of AKD through the ICCA program.

However, CAS 68955-37-3 is not included in this list.

In order that we can correct our records, please respond to this question as soon as you can via email to me and clarify whether Hercules intended for CAS 68955-37-3 to be included with the list of chemicals that were to have gone to the Global Producers of AKD.

Thank you for your prompt attention to this matter.

Sincerely,

Karen Hoffman

----- Forwarded by Karen Hoffman/DC/USEPA/US on 06/23/04 12:41 PM -----

NCIC HPV
Sent by: Michael Leczynski/DC/USEPA/US@EPA, Vanessa Ofner

05/11/04 01:53 PM

To: Barbara Williams/DC/USEPA/US@EPA, Larona Washington/DC/USEPA/US@EPA, Karen Hoffman/DC/USEPA/US@EPA, Karen Boswell/DC/USEPA/US@EPA, Diane Sheridan/DC/USEPA/US@EPA, Peter Wendolkowski/DC/USEPA/US@EPA, Deena Vann/DC/USEPA/US@EPA, Jeffrey Taylor/DC/USEPA/US@EPA, Karen Lannon/DC/USEPA/US@EPA, Renee Kearney/DC/USEPA/US@EPA, Jim Alwood/DC/USEPA/US@EPA
cc:
Subject: Hercules (201-15258)

- Commitment Scanned Files

This e-mail contains the following commitment letter, which was received from Hercules Incorporated.

1. The .gif format of the following item is attached:

201-15258 = c15258a.gif
c15258b.gif
c15258c.gif
c15258d.gif
c15258e.gif
c15258f.gif
c15258g.gif
c15258h.gif
c15258i.gif

2. The .pdf format of the following item is attached:

201-15258 = 201-15258.pdf

There are 10 files attached.

(See attached file: c15258a.gif)(See attached file: c15258b.gif)(See attached file: c15258c.gif)(See attached file: c15258d.gif)(See attached file: c15258e.gif)(See attached file: c15258f.gif)(See attached file: c15258g.gif)(See attached file: c15258h.gif)
(See attached file: c15258i.gif)(See attached file: 201-15258.pdf)

Please contact me if there are any questions or comments regarding these attachments. Thank you.

Michael Ofner
Contractor for EPA

c15258a.gif c15258b.gif c15258c.gif c15258d.gif c15258e.gif c15258f.gif c15258g.gif c15258h.gif c15258i.gif 201-15258.pdf

Attachment 3: <u>General Information Regarding the Manufacturing Process</u>

Hercules manufactures tallow fatty acid chlorides via halogenation of tallow fatty acid using phosphorus trichloride. The fatty acid chloride (FAC) intermediate is pumped into four tanks to separate by-products. Excess phosphorus trichloride is removed, organic and aqueous layers are separated, and the FAC intermediate is transferred to a process holding tank. The intermediate resides here, on average, only an hour or so. It is important to note that this not a storage tank as such but rather a "wide spot" in the manufacturing process prior to manufacture of the ketene dimer AKD via a semi-continuous process.

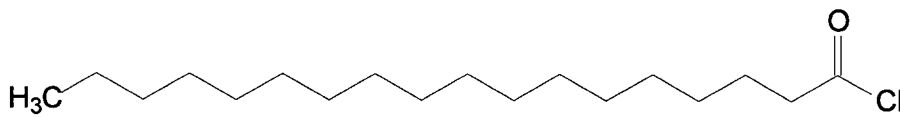
The FAC intermediate is semi-continuously removed from the holding tank into a reactor to make the final dimer product. The FAC is contained within contiguous tanks and transfer lines throughout the process. There are no steps that physically isolate or remove the intermediate from the process.

An estimated 40,000 pounds of dimer product may be produced during a single shift; thus the contents of the "holding" tank are quickly turned over. Hercules does not move the FAC intermediate from site to site. All FAC manufactured at a given site is consumer at that site.

Hercules considers this substance as a non-isolated intermediate with essentially no exposure. Thus, we feel it is not subject to the HPV program.

Attachment 4: Chemical and Environmental Fate of Fatty Acid Chlorides

The fatty acid (FA) from which CASRN: 68955-37-3; acid chlorides, tallow, hydrogenated, is generated is typically a mixture of C16 and C18 saturated (stearic and palmitic acids). Below is a diagram of a typical FA chloride, stearyl chloride in this case: CASRN 112-76-5.



Research indicated that FA chlorides will hydrolyze readily in the presence of moisture to hydrochloric acid and the corresponding fatty acid (see attachment 5: Bauer. S.T., and Curet. M.C., *Journal of the American Oil Chemists' Society*, Feb., 1947, The Hydrolysis of Fatty Acid Chlorides). This research indicated that stearyl chloride and pamityl chloride hydrolyzed almost completely within 4-5 hours.

Hercules argues that this hydrolysis will occur regardless of whether the FA chloride was introduced into the environment (such as waterways) or into a biological system (such as ingestion by an animal). Thus, the health and environmental effects of this fatty acid chlorides (and probably most other fatty acid chlorides) are determined by the health and environmental fate of the hydrolysis product. The health and environmental effects of hydrochloric acid are reasonably well known and predictable. The fatty acid hydrolysis products, stearic and palmitic in this case, are common fatty acids with many industrial and food uses, and are themselves, listed as HPV chemicals.

Thus, Hercules argues that the health and environmental effects of this specific HPV substance, CASRN 68955-37-3, will have already been established by virtue of known effects from hydrochloric HPV summaries prepared for stearic and palmitic acids.

acids are not available. Thus, as a result of their shortage of fats and oils during the war, the Germans used a linseed oil soap in the manufacture of Buna. This actually served a real function yet it did greatly slow down their production. Later when even this became unavailable they used synthetic fatty acid prepared by the oxidation of Fischer Tropsch paraffin.

Research work in this country has shown that synthetic rubber can be made from polyunsaturated acids and other low grade fatty acids at present production rates if special activators are used to compensate for the inhibiting effects. However, these types of rubber have never been tested extensively on a commercial scale and do introduce a number of new difficulties into the manufacturing operations.

Trends in the Manufacture of Soaps for Use in Making Synthetic Rubber

There has been a noticeable trend in the fatty acids or soaps used in the manufacture of synthetic rubber. At first distilled myristic and palmitic acid from spermaceti was used. This was replaced soon by distilled myristic acid from coconut fatty acids. When the supply of this became short, soap made from selectively hydrogenated tallows and greases was used. Large scale manufacture of GR-S necessitated larger quantities of soap. This was obtained first from high grade edible tallow and finally from hydrogenated oils, tallows, and greases.

Future developments point to the use of highly purified fatty acids or soaps having a definite ratio of the various fatty acids present. Crystallized acid are quite satisfactory and uniform in their activity For example, crystalline palmitic acid would be de sirable in certain cases while for others a crystallized high purity oleic acid free from polyunsaturate would be ideal. Improvement in crystallization proc esses and development of markets for the polyunsatu rated acids obtained as by-products will help to bring these things to pass. Proper economic analysis of the technological progress in the related fields will cer tainly determine the course of the future in this field

The author wishes to acknowledge the assistance obtained from the unpublished summaries and specifications contributed by the scientists and com panies who have participated in the synthetic rubber program.

REFERENCES

1. Fryling, C. F., and Harrington, E. W., Ind. Eng. Chem., *36*, 11 (1944).
2. McBain, J. W., and Soldate, A. M., J. Am. Chem. Soc., *64*, 155 (1942).
3. McBain, J. W., Private communication to Rubber Reserve, Marc 22, 1943.
4. Harkins, W. D., Heller, W., *et al.*, Private communication t Rubber Reserve, June 24, 1943.
5. Harkins, W. D., J. Chem. Phys., *13*, 381 (1945).
6. Willson, E. A., Private communication.
7. Fryling, C. F., Private communication to Rubber Reserve, 5-21-42
8. Cuthbertson, G. R., Coe, W. S., and Brady, J. L., Ind. Eng. Chem *38*, 975 (1946).
9. Hendricks, J. G., India Rubber World, *114*, 60 (1946).
10. Rubber Reserve specification limits for soap.
11. Pfau, E. S., Wilson, J. W., *et al.*, April to Nov., 1943, Privat communication to Rubber Reserve, March 13, 1944.
12. Semon, W. L., Private communication, March, 1941.
13. Rubber Age, *59*, 198 (1946); 1945 Report of Bureau of Ag. an Ind. Chem. of USDA.
14. Fryling, C. F., U.S.P. 2,366,325 to the B. F. Goodrich Company January 2, 1945.

The Hydrolysis of Fatty Acid Chlorides

S. T. BAUER and MAIZIE C. CURET
Southern Regional Research Laboratory[1]
New Orleans, Louisiana

IN the course of the preparation of a series of synthetic glycerides of known molecular configuration it was necessary to store the acid chloride (1) intermediates for various periods of time. The freshly distilled acid chlorides were stored in sealed glass ampoules and analyzed prior to use. After several months of storage under these conditions no appreciable hydrolysis could be detected. It was realized, however, that under commercial conditions of storage more or less hydrolysis might occur from the presence of moisture, and it appeared advisable, therefore, to determine the relative rates of decomposition of the more commonly used saturated and unsaturated fatty acid chlorides.

A search of the literature revealed little information on the relative rates of hydrolysis of acid halides. Velasco and co-workers (4, 6) investigated the velocities of hydrolysis of acetyl chloride, chloroacetyl chloride, propionyl chloride, and butyryl chloride. The degree of hydrolysis was determined by measuring the extent of diffusion of the reaction products into water and toluene at 25° C. and 45° C. These investigators reported that hydrogen ions do not catalyze any of the hydrolytic reactions of the chlorides, which would indicate that the mechanism of hydrolysis in this case is different from that of the esters and amides of the fatty acids. Similar results have bee reported by Velasco and Ollero (5) and by Karvé an Dolé (2, 3) with respect to the rates of hydrolysis of number of aromatic acid chlorides. The acid halide used by the latter investigators were dissolved i chloroform or benzene and shaken with water at constant rate. Hydrolysis was found to occur at th boundary between the two liquid phases at rate which were determined by diffusion of the reactant and reaction products across the interfacial boundary The rate constants were found to increase with in creasing concentration of acid halide. The hydro chloric acid formed during hydrolysis was found t exert no catalytic action. Conical flasks were said t favor the hydrolysis.

Since there are no available data on the hydrolys of the higher fatty acid chlorides, experiments wer made to determine the hydrolysis of a number o saturated and unsaturated fatty acid chlorides whe shaken with water for varying periods of time.

Experimental

Purification of the Fatty Acids and Preparation o Fatty Acid Chlorides. The saturated and unsaturate fatty acids, with the exception of octanoic and de anoic, were purified by the method described b Bauer (1). Commercial preparations of octanoic an

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE 1

Hydrolysis of Saturated Fatty Acid Chlorides

Time Minutes	Fatty acid chlorides					
	Octanoyl	Decanoyl	Lauryl	Myristyl	Palmityl	Stearyl
	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed
5	93.0	96.7	96.8	98.4	95.6	89.0
15	79.8	92.4	95.2	95.4	89.9	14.0
30	63.4	86.2	94.0	90.8	82.8	7.7
60	48.0	78.8	90.1	84.1	57.2	2.2
120	34.6	58.9	79.0	74.0	25.3	1.8
180	35.1	50.7	72.2	55.5	3.3	0.1
240	32.8	45.6	65.8	45.8	1.7	1.2
300	32.2	45.2	55.7	37.3	3.0	0.9
360	32.7	44.5	51.4	32.5	2.7	1.8
420	30.7	44.7	43.4	25.2	2.5	1.6
480	27.7	42.7	40.4	19.0	3.8	......
720	......	......	27.4	4.4	......	......
960	......	......	27.1	4.2	......	......
1440	......	......	16.9	3.4	......	......
1920	......	......	13.09	3.4	......	......
2160	......	......	13.99	......	......	......
2880	......	......	14.20	......	......	......

decanoic acids were fractionally distilled, and that fraction selected whose neutralization equivalent corresponded most nearly to the theoretical value.

The acid chlorides were prepared by reaction of the fatty acids with a suitable chlorinating agent according to previously described methods (1). The acid chloride was distilled and sealed in glass ampoules until used. The purity of each preparation was determined by weighing a one-gram sample of the acid chloride into a 50-ml. glass-stoppered Erlenmeyer flask to which was added 20 ml. of a 20% aniline-ether solution. After the reaction was completed, 2 ml. of concentrated hydrochloric acid was added to convert the excess aniline to the hydrochloride. The ether was removed by evaporation on the steam bath and the aniline hydrochloride and mineral acid were removed by washing the anilide repeatedly with distilled water. The free fatty acid content of the anilide solution was determined by dissolving the product in 25 ml. of hot neutral alcohol and titrating the solution with 0.1 N sodium hydroxide. Analysis of the acid chlorides used in this work indicated a purity of 99.2% or better on the assumption that free fatty acid was the only impurity present.

Hydrolysis of the Fatty Acid Chlorides. A portion (approximately 0.9-1.0 g.) of acid chloride was weighed into a 50-ml. glass-stoppered Erlenmeyer [illegible] which was placed on a mechanical agitator. A [illegible] bead was added to the flask and 5 ml. of dis-[illegible] water was added from a pipette. The agitator [illegible] was a modification of Camp's shaking apparatus [illegible] imparted a planetary motion to the contents of [illegible] flasks through a pulley-driven shaking platform.

The acid chloride-water mixture was shaken at room temperature (25° C.) for various intervals of time after which the reaction was stopped by the addition of 10 ml. of a 20% aniline-ether solution to convert the unhydrolyzed portion of acid chloride to the corresponding anilide.

The free fatty acid content of the anilide-fatty acid mixture was determined by titration with one-tenth normal sodium hydroxide solution. Since any free fatty acid which may have been present in the original chloride is titrated along with that produced by hydrolysis, the observed value of the latter must be corrected by subtraction of the previously determined value for the former.

TABLE 2

Hydrolysis of Unsaturated Fatty Acid Chlorides

Time Minutes	Fatty acid chloride		
	Elaidyl	Oleyl	Linoleyl
	Mole % unhydrolyzed	Mole % unhydrolyzed	Mole % unhydrolyzed
5	97.6	96.9	97.2
15	94.8	96.9	89.8
30	91.1	95.2	82.4
60	88.0	67.8	73.0
120	78.4	29.7	64.0
180	71.1	21.5	50.5
240	62.5	18.9	46.0
300	50.4	20.7	44.0
360	47.7	21.5	46.6
420	39.2	21.2	45.9
720	12.9	16.3	......
960	1.3	......	......
1440	1.5	......	......
1920	......	11.98	......
2160	......	......	......
2880	0.5	......	......

In order to compare the relative rates of hydrolysis of the acid chlorides it is necessary to express the results on a mole percentage basis. This may be done by means of the following equation:

Mole per cent of unhydrolyzed acid chloride equals

$$\frac{\text{moles original acid chloride} - (\text{moles NaOH} - \text{moles free fatty acid in original acid chloride})}{\text{moles original acid chloride}} \times 100$$

or

$$\frac{\dfrac{W_s - W_a}{\text{M. W. chloride}} - \left(\dfrac{\text{ml. NaOH} \times \text{normality}}{1000} - \dfrac{W_a}{\text{M. W. acid}}\right)}{\dfrac{W_s - W_a}{\text{M. W. chloride}}} \times 100$$

where W_s = weight of sample, and W_a = weight of free fatty acid in the original sample of acid chloride used for hydrolysis.

TABLE 3

Specific Reaction Rate Constants for Hydrolysis of Fatty Acid Chlorides at 25° C.*

Reaction time	Fatty acid chlorides								
	Octanoyl	Decanoyl	Lauryl	Myristyl	Palmityl	Stearyl	Elaidyl	Oleyl	Linoleyl
Minutes	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$	$k \times 10^3$
[illegible]	14.52	6.71	7.54	3.22	9.00	23.31	4.86	2.21	5.68
[illegible]	15.04	5.27	3.28	3.14	7.10	131.1	3.56	2.10	7.17
[illegible]	15.19	4.95	2.06	3.22	6.29	85.5	3.11	1.64	6.45
[illegible]	12.23	5.06	1.74	2.89	9.31	......	2.13	6.48	5.25
[illegible]	8.85	4.41	1.96	2.51	11.45	......	2.03	......	5.64
[illegible]	......	3.77	1.81	3.27	......	......	1.90	......	3.80
[illegible]	......	......	1.75	3.25	......	......	1.96	......	......
[illegible]	......	......	1.95	3.29	......	......	2.28	......	......
[illegible]	......	......	1.85	3.12	......	......	2.06	......	......
[illegible]	......	......	1.99	3.28	......	......	2.23	......	......
[illegible]	......	......	1.89	3.46	......	......	......	......	......
[illegible]	......	......	1.80	4.35	......	......	2.84	......	......
[illegible]	......	......	1.36	3.30	......	......	4.51	......	......
[illegible]	......	......	1.24	2.38	......	......	......	......	......

[illegible]nstants determined only to point of apparent equilibrium.

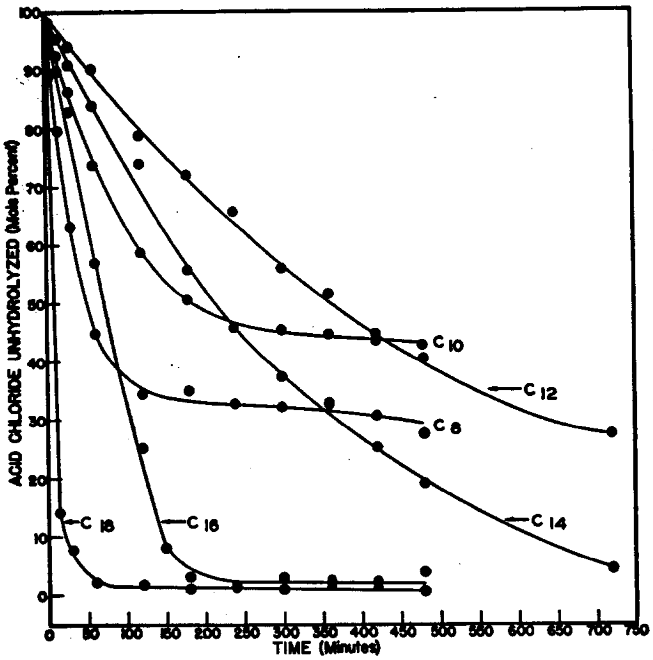


Fig. 1. Hydrolysis of saturated acid chlorides in water at 25° C.

Discussion of Results

Data relative to the hydrolysis of the chlorides of the even-numbered saturated fatty acids from caprylic to stearic are given in Tables 1 and 3 and graphically in Figures 1 and 3. It is evident from the curves in Figure 1 that of the chlorides investigated lauryl chloride is the most resistant and stearyl chloride the least resistant to hydrolysis. Stearyl chloride was essentially completely hydrolyzed after shaking with water for two hours at 25° C., whereas lauryl chloride was hydrolyzed to the extent of only 21% under the same conditions.

Experiments in which weighed amounts of acid chlorides were shaken with 0.1 N hydrochloric acid solution showed that the hydrogen ion had little if any effect on the rate of hydrolysis. Addition of small amounts of free fatty acids to the acid chloride prior to hydrolysis likewise appeared to have no effect on the rate of decomposition of the chloride.

Data with reference to the hydrolysis of the unsaturated fatty acid chlorides are given in Tables 2 and 3 and graphically in Figures 2 and 4. It is apparent from Figure 2 that elaidyl chloride is more resistant to hydrolysis than either oleyl or linoleyl chlorides. The linoleyl and oleyl chlorides hydrolyze at approximately the same rates during the first hour, but thereafter oleyl chloride hydrolyzes more rapidly than linoleyl chloride.

From calculations of specific reaction rates (Table 3) and plots of the logarithms of concentration of acid chloride vs. time, corresponding to various times of reaction (Figures 3 and 4), it appears that acid chlorides undergo hydrolysis in water to a point of apparent equilibrium. This equilibrium appears to take place after about 15 minutes of hydrolysis for stearyl chloride, 30 minutes for octanoyl chloride, 60 minutes for decanoyl and palmityl chlorides, 960 minutes (16 hours) for lauryl chloride, and 1,440 minutes (24 hours) for myristyl chloride. The unsaturated acid chlorides reach the point of equilibrium at 60 minutes for oleyl chloride, 180 minutes for linoleyl chloride, and 960 minutes for elaidyl chloride.

Several hypotheses may be advanced to explain th difference in the rates of hydrolysis between the C_8 t C_{12} and the C_{12} to C_{18} saturated acid chlorides and th apparent equilibrium reached in the case of the shorte chain compounds. The decrease in the reaction rate of the fatty acid chlorides from C_8 to C_{12} may be a tributed to decreasing activity of the acid chloride with increasing chain length. The increasing reactio rates of the fatty acid chlorides from C_{12} to C_{18} probably due to the increase in melting point an decrease in solubility of the fatty acids, liberated b hydrolysis, in the unhydrolyzed fatty acid chlorid This would result in a more complete withdrawal o the reaction products from the interface at which th reaction occurs. The fact that the hydrolysis of th shorter chain fatty acid chlorides reaches an appare equilibrium before the acid chloride is complete hydrolyzed indicates the probable formation of mono-molecular layer of free fatty acid at the inte face which inhibits contact between the unhydrolyze acid chloride and water. Further experimental dat would be required to substantiate these hypotheses.

Summary

Fatty acid chlorides of octanoic, decanoic, lauri myristic, palmitic, stearic, oleic, elaidic, and linole acids were hydrolyzed at 25° C. in water and th amounts of unchanged acid chlorides determine after different periods of reaction.

Contrary to expectations, the chlorides of the longe chain fatty acids, palmitic and stearic, reacted at more rapid rate than the chlorides of the shorter chai fatty acids. Lauryl chloride appears to be more resis

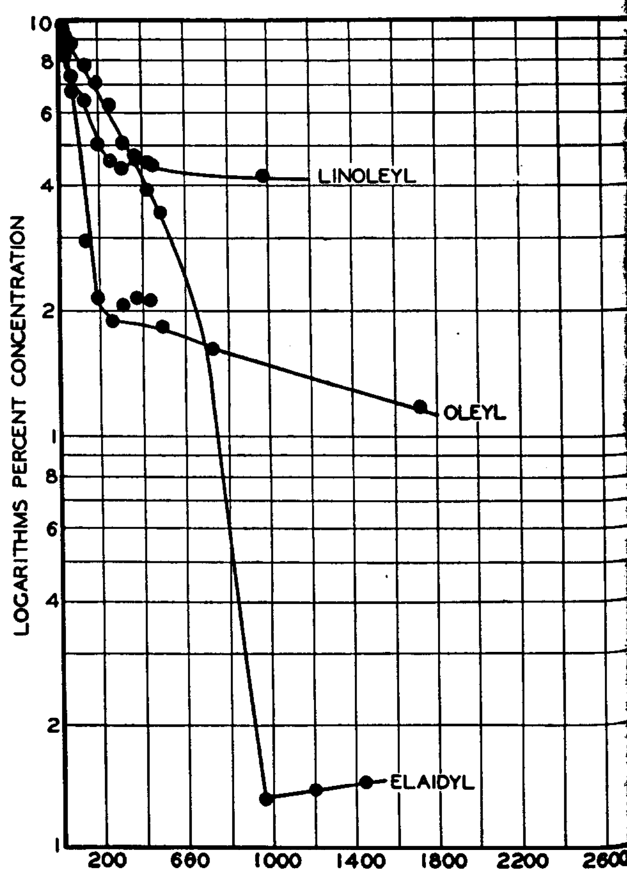


Fig. 2. Hydrolysis of unsaturated acid chlorides in wate at 25° C.

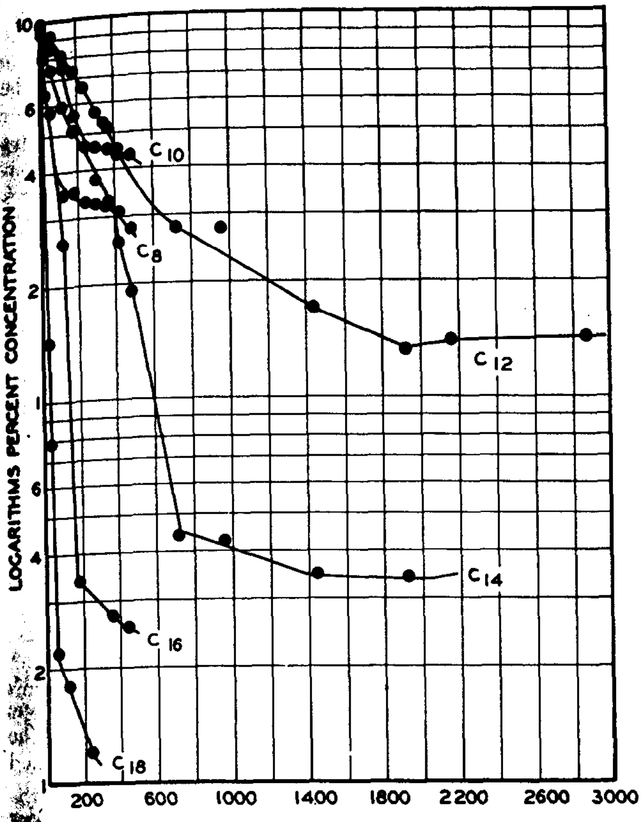


FIG. 3. Hydrolysis of saturated acid chlorides in water at 25° C.

ant to hydrolysis than either the chlorides of the lower molecular weight octanoic and decanoic acids or the chlorides of the higher molecular weight myristic to stearic acids.

The chlorides of the unsaturated acids, oleic, elaidic, and linoleic, are hydrolyzed less rapidly than stearyl chloride. However, elaidyl and myristyl chlorides exhibit the same relative rates of hydrolysis during the first two hours of reaction. Myristyl chloride hydrolyzes more rapidly than elaidyl chloride after the first two hours.

The addition of either hydrochloric acid or free fatty acids to the reaction mixture was found to have no pronounced effect on the hydrolysis of the acid chlorides.

REFERENCES

1. Bauer, S. T., Oil & Soap, 23, 1-5 (1946).
2. Karvé, Dinakar and Dolé, Krishnaji Khando, J. Indian Chem. Soc., 12, 733-9 (1935).
3. Karvé, Dinakar and Dolé, Krishnaji Khando, J. Univ. Bombay, 7, pt. 3, 108-25 (1938).
4. Velasco, J. R., and de la Borbolla, J. R., Anales soc. españ. fís. quím., 34, 179-97, 603-636 (1936).
5. Velasco, J. R., and Ollero, A., *Ibid.*, 34, 911-18 (1936).
6. Velasco, J. R., and Ollero, A., *Ibid.*, 35, 76-83 (1937).

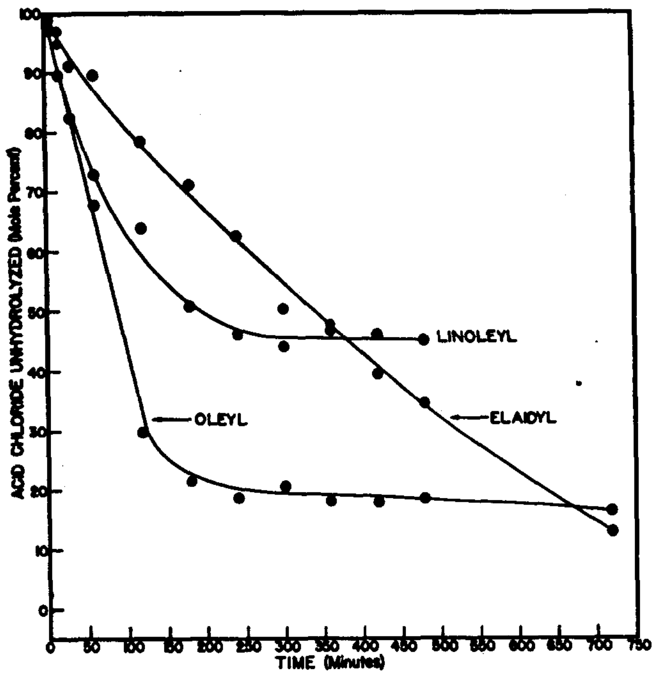


FIG. 4. Hydrolysis of unsaturated acid chlorides in water at 25° C.

A Study of Rancidity of Olive Oils

S. A. KALOYEREAS
Louisiana State University, Baton Rouge, Louisiana

INVESTIGATION of the problem of rancidity is rendered difficult by the fact that the ultimate standards to which all data must be referred are based on taste and smell. Among the aims of these experiments were: a) the comparison of the various known chemical tests for rancidity of fats and oils with the organoleptic test for the purpose of selecting the most reliable one for further use as a standard of reference; b) determination whether olive oils from different localities have different susceptibility to fat oxidation and the study of the effect of various factors and treatments upon such susceptibility to oxidation; and c) determinations whether anise seeds and mustard seeds have antioxidant value for olive oil.

The methods used were the following:

Oxidizability-value developed by Issoglio and modified by Kerr (1), which gives the amount of water-soluble oxidizable substances expressed in O_2/100 gm. oil.

The Kreis (2) test which is based on the presence in rancid fats of epihydrin aldehyde, an oxidation product of acrolein. It consists in the treatment of the oil with hydrochloric acid and a solution of phloroglucinol in ether.

Fellenberg (3) test based on the presence of aldehydes in the oxidized fats. Vintilesco and Popesco (4) test based on the presence of peroxides and oxides formed during the development of rancidity.

The Wheeler's (3) iodimetric method of determining the peroxides formed in rancid fats.

The last method was carried out as follows: five g. of olive oil were dissolved in 50 ml. of a mixture of glacial acetic acid and chloroform (3:2 by volume), after which one ml. of saturated potassium iodide solution was added. The mixture was stirred by giving a rotary motion to the flask. Exactly one minute after addition of the potassium iodide, 100 ml. of water were added and the liberated iodine titrated with 0.01 N sodium thiosulphate, using starch as